A.A. Korotkov (Leningrad) on catalytic polymerization.

V.V. Korshak, Member-Correspondent of the USSR Academy of Sciences (Moscow) on syntheses of phosphor containing polymers.

Professor G.Kh. Kamay (Kazan') on syntheses of certain unsaturated ethers of phosphinous acids.

Academician O. Vikhterle and Professor Vesely (Czechoslovakia) on cation polymerization of olefines.

K.A. Andriyanov, Member-Correspondent of the USSR Academy of Sciences (Moscow) on the elaboration of a new class of thermostable polymers.

Professor Z.A. Rogovin on the qualities of methyl carbonic ether of celluloses.

Professor V.I. Ivanov on cellulose qualities and their application in chromatography.

Professor Van-Yu- Khay (China) on the titration of terminal groups of polycaprolactams.

Academician V.A. Kargin (Moscow) and G.S. Markova on the orientation and crystallization of polymeric chains and their disposition.

Academician P.A. Rebinder (Moscow) and Professor G.V. Vinogradov on methods characterizing the viscous elastic qualities

of polymeric solutions and the application of new rheological and optical polarization methods

Professor K. Hess (Gess) from the Federal German Republic, on submicroscopic structures of polymers.

Yu. S. Lazurkina (Moscow) and Ye.V. Kuvshinskiy (Doctors of Physics-Mathematics) on the qualities of polymeric glass and the mechanics of glass formation of high molecular combinations.

Professor Chen-Bao-Kun (China) on viscous plastic qualities of natural rubber.

Professor S. Goreyko (Poland) on polyvinyl chloride qualities.

Professor Z.A. Rogovin on investigations in obtaining fluorine containing synthetic carbon chain fibres.

Professor Kh. Simionesku (Rumania) on fractionation of cellulose.

Professor T. Rabek (Poland) on the qualities of ion-exchange resin.

The second Vuz Conference on Embryology took place from 28th January to 5th February at the Moskva University. About 600 participants were present, and 150 reports were read. Present also were Professor G. Muller (Halle, GDR) and A. Kelyus (Krakow, Poland).

The resolution of the Conference contained recommendations to increase theoretical work on the problems of individual develop-

ment of organisms. The creation of an embryology periodical was suggested.

The Moscow University convened the first Vuz Conference on Biochemical and Physico-chemical Principles of the Biological Action of Radiation in February 1957. About 700 participants were present.

An introductory paper was read by Professor B.N. Tarusov (Moscow) dealing with the biological action of ionizing radiations. Professor A.M. Kuzin made a report on radiotonal biochemical aspects. Other reports were:

Professor M.N. Meysel' (Moscow) on the effect of radiation on various components of the cells of micro-organisms. N.P. Dubinin, Member-Correspondent of the USSR Academy of Sciences (Moscow), on radiation genetics.

The resolution of the conference dealt with the creation of a course in radiation genetics, to be included into the program of genetics and biophysics. The conference decided moreover to invite qualified specialists to investigate the biological action of radiation. It was decided to apply at the Ministry of Higher Education for the organization of courses dealing with working methods of isotopes.

A scientific conference dealing with problems of the structure of organic combinations, took place from 14th to 16th January 1957 at the Kazan' University. More than 200 participants were present and 19 reports were delivered on subjects of theoretical organic chemistry (tautomerism, geometry of organic molecules, etc). The conference stated the successful development of the theory of A.M. Butlerov, and the necessity to resolve problems of modern organic chemistry through physical research methods, such as infrared spectroscopy, spectroscopy of the combined dispersion of light and the methods of magnetic resonance, introduced by Ye.K. Zavoyskiy.

A conference on the Economical Efficiency of New Techniques in Construction was convened in January 1957 by the Moskva Institute of Engineering and Economy, together with the economic departments of Gosstroy SSSR and the Scientific-Technical-Society of the USSR Construction Industry. About 430 participants heard 46 reports. Professor, Doctor of Technical Sciences, L.I. Onishchik (Moscow) spoke on "Problems of Wall Building From the Point of View of Economical Efficiency".

Professor Ye.I. Varenik, Doctor of Technical Sciences (Moscow), spoke on "The Evaluation of th Economical Efficiency of Constructions With Selected Sections".

V.P. Lagutenko, chief engineer of the Mosgorispolkom Department of Architectural Planning, on "Rational Solutions in the Construction of Buildings - A Principle of Economical Building".

In May 1957 a conference of leading workers of soil division work in USSR was held at the Moskva University.

Representatives of 8 universities and 2 agricultural institutes were present, as well as members of the USSR Academy of Sciences and the Soil Institute imeni Dokuchayeva of the USSR Academy of Sciences.

Eight reports and 3 information papers relating to the principles and situation of soil division in many Soviet areas were read. The conference decided to develop this work, and to apply at the Ministry of Higher Education to convene a conference on this subject in January 1958.

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MEDVEDEV S.S.

68-12-23/25

AUTHOR: Liplavk, I.L.

TITLE: All-Union Scientific-technical Conference on the Application of Radio-active and Stable Isotopes and Radiations in the National Economy and in Science (Vsesoyuznaya nauchno-tekhnicheskaya konferentsiya po primeneniyu radioaktivnykh i stabil'nykh izotopov i izlucheniy v narodnom khozyaystve i nauke)

PERIODICAL: Koks i Khimiya, 1957, No.12, pp. 53 - 54 (USSR)

ABSTRACT: This is a report on the conference couched in general terms. The conference was convened by the Ac.Sc. USSR and the Chief Directorate for Utilising Atomic Energy at the Council of Ministers of the USSR. About 4 000 specialists participated and also a large number of guests from Soviet bloc countries, France and USA. At the fourteen sections of the conference, about 500 papers were read. The paper of S.S. Medvedev, Corresponding Member of the Ac.Sc. USSR, was devoted to the prospect of utilisation of nuclear radiations in chemistry. By means of nuclear radiation it has been possible to achieve, under certain laboratory conditions, direct synthesis of aniline from a mixture of benzole with ammonia, and of phenol from a mixture of benzole with water. By means of radiolysis, it is possible to achieve oxidation of substances which do not oxide

Cardl/4

All-Union Scientific-technical Conference on the Application of Radioactive and Stable Isotopes and Radiations in the National Economy and in Science.

under normal conditions. Of interest, also, were the papers on radiation chemistry of the solid body - furthermore, the so-called "cold" cracking. By passing of crude through a radioactive cobalt tube, it is possible to obtain directly high-quality gasolines. Much attention was paid to investigating nuclear radiation for controlling automation of technological processes, to developing methods and apparatus for radiometry and dosimetry of nuclear radiations. On the basis of the presented papers and the discussions, it is evident that the Soviet Union is holding its own and is even in advance of other countries as regards the development of new instruments, but lags far behind as regards industrial manufacture of such instruments. Only density meters, level meters and gamma-defectoscopy apparatus are being series produced. A major achievement is the development of a new instrument, the concentration meter, which is based on nuclear radiation spectroscopy and permits solving, for instance, continuous control of the composition of complex mixtures. The coke-chemical industry lags far behind other industries in utilising nuclear radiations.

All-Union Scientific-technical Conference on the Application of Radio-active and Stable Isotopes and Radiations in the National Economy and in Science

A considerable part of the papers was devoted to the perfection of known methods, particularly as regards prospecting for oil. Recently, "gamma-gamma logging" was developed which permits coreless investigation of a cross-section of coal seams, determining the thickness of seams, the degree of ash content and also, very approximately, the grade composition of the coals. Interesting papers were read on using radio-active isotopes for studying the effects of explosions in mining. Personnel of the Institute of Mined Fuels Ac.Sc. USSR (Institut goryuchikh iskopayemykh AN SSSR) reported on using radioactive radiations for coal beneficiation and for monitoring coal quality; the method is based on the weakening of the soft gamma-radiation as a function of the density and composition of coal particles. The Institute developed and manufactured a model of a radiometric separator for automatic sorting of bits of coal from rock for dimensions of up to 100 mm. A rapid method was also developed for determining the ash content of coal by means of ordinary counters. All problems related to the manufacture of radioactive and of

'EDEV, S.S.

MEDVEDEV S.S.

KARGIN, V.A.

5(3) p4 PHASE I BOOK EXPLOITATION SOV/1589

Akademiya nauk SSSR.

Khimiya bol'shikh molekul; sbornik statey (Chemistry of Large Molecules; Collection of Articles) Moscow, Izd-vo AN SSSR, 1958. 299 p. (Series: Akademiya nauk SSSR. Nauchno-populyarnaya seriya) 30,000 copies printed.

Compiler: G.V. Sklovskiy; Resp. Ed.: A.V. Topchiyev, Academician; Ed. of Publishing House: V.A. Boyarskiy; Tech. Ed.: I.N. Guseva.

PURPOSE: This book is intended for a wide circle of readers including those who have had no training in chemistry. It can also serve as amanual for propagandists, teachers, and journalists.

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Chemistry of Large Molecules (Cont.) SOV/1589

COVERAGE: This collection of articles reflects the trend for the future development of the Soviet chemical industry as indicated by the May plenary session of the Central Committee of the Communist Party within the framework of the new Seven Year Plan. These articles were published in newspapers and journals. The authors, scientists and industry workers, developed the theme of accelerated development of the chemical industries, and sciences, with stress on the manufacture of synthetic fibers, plastics, and other materials. Some of the articles were abridged, revised, or enlarged. The articles were selected so as to give an adequate survey of the chemistry and technology of high-molecular-weight compounds and their use in industry, agriculture, and in the manufacture of consumers' goods. Mentioned are raw materials for the production of polymers. This book belongs to the popular-science series of the Academy of Sciences. Similar volumes are intended for future publication. No references are given.

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MEDVEDEV, S. S. and A. N. PRAVEDNIKOV

"The Formation of Side Chains With the Irradiation of Polyethlenes by Ionizing Radiation" p. 269

Truly Transactions of the First Conference on Radioaction Chemistry, Moscow, Izd-vo AN SSSR, 1958. 330pp.
Conference -25-30 March 1957, Moscow

BAKH, N.A., prof., otvetstvennyy red.; MEDVEDEV, S.S.; VESELOVSKIY, V.I., prof.; DOLIN, P.I., doktor khim. nauk; MILLER, N.B., kand. khim. nauk; TSETLIN, B.L., kand. khim. nauk; TRIFONOV, D.N. red. izd-va; BUGAYENKO, L.T., red. izd-va; MOSKVICHEVA, N.I. tekhn. red.

[Transactions of the First All-Union Conference on Radiation Chemistry]. Vsesoiuznoe soveshchanie po radiatsionnoi khimii. 1st, Moscow, 1957. Trudy... Moskva, Izd-vo Akad. nauk SSSR, 1958. 330 p. (MIRA 11:7)

1. Chlen korrespondent Akademii nauk SSSR (for Medvedev).
(Radiochemistry--Congresses)

MEDVEDEV, S. S., (Physico-Chemical Institute im L. Ya. Karpov)

"Prospects of Using Nuclear Radiation in Chemistry"

[illegible] and Radia[illegible]ion in Chemistry, Collection of Reports at the [illegible]ation Sci.Tech. Conf. on the Use of Radioactive and Stable Isotopes and Radiation in National Economy and Science. Moscow, Izd-vo Akad Nauk, [illegible],

This volume publishes reports of the [illegible] Section of the [illegible] Conf on the Use of Stable Isotopes and Radia[illegible] [illegible] and the National Economy held in [illegible] [illegible] ation for Utilization of Atomic Energy under Council of Ministers [illegible] Union, [illegible].

PRAVEDNIKOV, A. N., YING SHENG KANG, MEDVEDEV, S. S.

"On the Mechanism of Cross-Linking of Polymer Chains Under Gamma-Irradiation."

paper to be presented at 2nd UN Intl.' Conf. on the peaceful usess of Atomic Energy, Geneva, 1 - 13 Sept 58.

MEDVEDEV, S.S.; KHOMIKOVSKIY, F.M.; SHEYNKER, A.P.; ZABOLOTSKAYA, Ye.V.; BEREZHNOY, G.D.

Some laws governing emulsion polymerization. Probl.fiz.khim. no.1:5-17 '58. (MIRA 15:11)

1. Laboratoriya polimerizatsionnykh protsessov Nauchno-issledovatel'skogo fiziko-khimicheskogo instituta im. Karpova.

(Polymerization) (Emulsions)

MEDVEDEV S. S.

64-1-18/19

AUTHOR: Malyusov, V. A.

TITLE: Scientific Conference at the Institute for Physical Chemistry Imeni L. Ya. Karpov
(Nauchnaya konferentsiya v Fiziko-khimicheskom institute imeni L. Ya. Karpova)

PERIODICAL: Khimicheskaya Promyshlennost', 1958, Nr 1, pp. 56-56 (USSR).

ABSTRACT: At the end of November, 1957, a meeting of the scientific session of the scientific council took place in the above mentioned institute in honour of the 40th anniversary of the great socialist October Revolution. 19 contributions of the most interesting works carried out of lately in this institute were delivered. The corresponding member of the AN USSR, professor S. S. Medvedev, gave a report on the investigation of the general rules governing the emulsion polymerization. The active member of the AN USSR, professor V. A. Kargin reported on new observations in structural polymers. The corresponding member of the AN USSR, professor K. A. Kocheshkova reported on investigations in the field of organic lithium compounds. The corresponding member of the AN USSR, N. A. Kazarnovskiy,

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Scientific Conference at the Institute for Physical Chemistry Imeni L. Ya. Karpov

reported on peroxide compounds of the alkaline metals, professor A. I. Shatenshteyn on the isotopic reactions with deuterium in anhydrous solutions, professor P. P. Shorygin on the interaction of the substituents in molecules of organic compounds, D. N. Shirogin on the nature and effect of the hydrogen- and metal element binding, professor B. F. Ormont on the importance of the solid phases, professor G. S. Zhdanov reported on the work of the electronic computing machine "Kristall" and demonstrated it. V. L. Karpov reported on the investigations of the radiation stability of high polymers, professor V. I, Veselovskiy on the mechanism of the radiation-electrochemical processes, professor M. A. Proskurnin on the sensitization of radiation-chemical reactions, professor S. Ya. Pshezhetskiy on the oxidation of nitrogen under ionizing radiations, professor N. N. Tunitskiy on the molecule- and ionic dissociation in the mass spectrometer, A. Kh. Breger on sources of nuclear radiations, professor Ya. M. Kolotyrkin on electrochemical investigations of metals, the corresponding member of the AN USSR professor N. M. Zhavoronkov reported on the process of steady and unsteady mass transport in the absorption and rectification, professor

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Scientific Conference at the Institute for Physical Chemistry Imeni L. Ya. Karpov. 41-1-18/19

M. I. Temkin and L. E. Apel'baum on the chain characteristics of heterogeneous catalytic reactions and professor G. K. Boreskov reported on: "Some Questions of Catalyst Selection." There are no references.

AVAILABLE: Library of Congress.

1. Chemical rese...h-USSR 2. Scientific research-USSR

Card 3/3

MEDVEDEV, S. S. (Karpov, USSR)

"Polymerization through Irradiation."

paper presented at the Intl. Conference on Radioisotopes in Scientific Research in Paris, 19-20 Sept 1957.

Angewandte Chemie, No. 3, 1958.

AUTHORS: Razumovskiy, S. D., Medvedev, S. S. SOV/62-58-8-10/22

TITLE: Kinetics of the Reaction of Cumene Hydrogen Peroxide With Triethylene Tetraamine in the Presence of Iron Salts in Aqueous Solutions (Kinetika reaktsii gidroperekisi kumola s trietilentetraaminom v prisutstvii soley zheleza v vodnykh rastvorakh)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1958, Nr 8, pp. 973-980 (USSR)

ABSTRACT: Lately the methods of the arrangement of processes with radicals by means of redox reactions have been employed more and more in the production of high-molecular products. The peroxide compounds are the oxidation components used most. In publications there exist various papers on this subject (Refs 1-9), among them also that by Ohrr and Williams (Orr and Vil'yams, Refs 8,9). The papers published hitherto have, however, not at all explained the role played by the iron in the reaction (and the dependence of the rate of reaction on the concentration of the iron). The present paper deals with the explanation of this problem. The experiments demonstrated that the reaction between cumene hydrogen peroxide and triethylene tetraamine takes

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Kinetics of the Reaction of Cumene Hydrogen Peroxide With Triethylene Tetraamine in the Presence of Iron Salts in Aqueous Solutions

place only in the presence of iron. The activity of the iron salts mainly depends on the conditions of the experiment, and may be explained by the salt hydrolysis. It was also found that the amine has the capability of reducing the iron salts in acid as well as in alkaline medium. The course of the reaction with respect to all reaction components was determined more accurately. The activation energy of the entire reaction was calculated. The rules governing the change of the concentration of hydroperoxide were determined. Finally the constants of the summary equation were calculated. There are 7 figures, 2 tables, and 21 references, 5 of which are Soviet.

ASSOCIATION: Moskovskiy Institut tonkoy khimicheskoy tekhnologii im. M. V. Lomonosova (Moscow Institute of Fine Chemical Technology imeni M. V. Lomonosov)

SUBMITTED: January 14, 1957

AUTHORS: Razumovskiy, S. D., Medvedev, S. S. SOV/72-58-9-11/25

TITLE: Styrene Polymerization in Emulsion Under the Influence of the Initiating System Cumene-Triethylene-Tetramine Hydroperoxide (Polimerizatsiya stirola v emul'sii pod vliyaniyem initsiiruyushchey sistemy gidroperekis' kumola-trietilen-tetramin)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye Khimicheskikh nauk, 1958, Nr 9, pp 1088 - 1093 (USSR)

ABSTRACT: The initiation of polymerization by oxidation and reduction in aqueous emulsions has found wide-spread use. The system hydroperoxide-polyethyleneamine serves as an example of the oxidation-reduction system. Its polymerization initiating effect proved to be sufficient in the co-polymerization of divinyl with styrene. The reaction between the hydroperoxides and polyamines has been the subject of countless investigations (Refs 5-8). In the present paper the authors are concerned with the kinetics of the reaction between cumene hydroperoxide and triethylenetetramine in an emulsion

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medium, as well as the polymerization kinetics of the hydroperoxide-polyethyleneamine system already mentioned. It was found that the rate of reaction depends upon the concentration of the reactants. On the basis of the experimental results obtained several considerations arise in regard to the mechanism of the reaction. The kinetics of the polymerization reaction of styrene in emulsion and under the cumene-hydroperoxide-triethylene-tetramine system were investigated. It was found that the polymerizing effect of this system is actually very small. There are 11 figures and 8 references, 3 of which are Soviet.

ASSOCIATION: Moskovskiy institut tonkoy khimicheskoy tekhnologii im.M.V.Lomonosova (Moscow Institute for Fine Chemical Technology imeni M.V.Lomonosov)

SUBMITTED: February 7, 1957

MEDVEDEV, S. S.
[redacted],

"Problems of the Polymerization of Ethylene in its Gaseous and Liquid Phase."

report presented at the UNESCO Conf. on Utilization of Radioactive Isotopes in Scientific Research, Paris, 9-20 Sept 1958?
Vestnik AN SSSR, V. 28, No. 1, 1958, (author Vinogradov, A. P.)

AUTHORS: Lipatova, T. E., Gantmakher, A. R., Medvedev, S. S. SOV/76-32-9-13/46

TITLE: ~~The Catalytic~~ Copolymerization of Unsaturated Compounds (Sovmestnaya kataliticheskaya polimerizatsiya nenasyshchennykh soyedineniy) II. The Copolymerization of Isoprene and α-Methyl Styrene (II. Sovmestnaya polimerizatsiya izoprena s α-metilstirolom)

PERIODICAL: Zhurnal fizicheskoy khimii, 1958, Vol 32, Nr 9, pp 2029 - 2034 (USSR)

ABSTRACT: These compounds were polymerized in an ethyl chloride solution at 0°C using tin (IV) chloride as a catalyst. The composition of the copolymers formed was determined from the volume decrease during the polymerization and by means of infra-red spectroscopy. The spectra are reproduced in figures 1,2, and 3. The molecular weights were determined by the osmotic method (Table 2). Diagrams show the course of the polymerization of α-methyl styrene alone (Fig 5) and of the copolymerization of isoprene and α-methyl styrene. The work shows that three components, isoprene, α-methyl styrene, and a product of copolymerization with inner

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double bonds take part in the polymerization reactions. Steric factors are important in the reaction between the tertiary carbonium ion and monomers. α-methyl styrene is considerably more reactive than isoprene. The initial reaction rate in the polymerization of the α-methyl styrene is decreased by the introduction of isoprene into the system. This is explained by the fact that various complex monomer-catalysts are formed. This formation reduces the concentration of the complex formed by the tin (IV) chloride with α-methyl styrene, which is the more active of the two monomers in initiating carbonium polymerization. There are 7 figures, 2 tables, and 2 references, 2 of which are Soviet.

ASSOCIATION: Fiziko-khimicheskiy institut im.L.Ya.Karpova, Moskva (Moscow Physical-Chemical Institute imeni L.Ya.Karpov)

SUBMITTED: April 4, 1957

20-119-...

AUTHORS: Ludvig, Ye. B., Gantmakher, A. R., Medvedev, S. S., Corresponding Member, Academy of Sciences, USSR

TITLE: Some Peculiarities of the Carbonium-Polymerization of the Styrene-α-Methylstyrene System (Nekotoryye osobennosti karbonivevoy polimerizatsii sistemy stirol-α-metilstirol)

PERIODICAL: Doklady Akademii Nauk SSSR, 1958, Vol. 119, Nr 1, pp. 90-93 (USSR)

ABSTRACT: The present paper is devoted to the investigation of a common cationic polymerization of the above-mentioned substances. In the earlier first investigation by the authors a rapid acceleration of the styrene-polymerization in the presence of small additions of α-methyl-styrene was observed. Now the dependence of the common polymerization on the composition of the initial mixture was investigated, and compositions of corresponding polymers together with the molecular weights determined. The obtained results were compared with the results of the separate polymerization. $SnCl_4$ in a solution of ethyl chloride at 0°C was used as catalyst. The curves (figure 1) obtained for various initial relations of the

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monomers show that in the concentration range from 0,7 to 1,7 Mol for α-methylstyrene (at a total concentration of the monomers of 2,5 Mol/liter) the polymerization under review takes place without an induction period with a gradually decreasing velocity. The composition of the co-polymers with those of the initial mixtures is given in table 1 which shows that the co-polymers are highly enriched with α-methylstyrene as more active component. The product of the co-polymerization-constants in this system is less than 1 (references 1,2). The steric effect manifests itself in a separate polymerization of α-methylstyrene which is confirmed by the reduced thermal effect of its polymerization (ref. 3). The molecular weight of the polymers are given in table 2. The kinetic curves of the domain of the additions of small quantities of the more active component (figure 2) are the most interesting. The intensive effect of an increase in polymerization velocity in the course of time is characteristic here. It begins at a certain stage of the polymerization which is characteristic of every given relation of the polymers. The maximum velocity was observed in a relation of 10 Mol styrene: 1 Mol α-methylstyrene. With increasing

concentration of the catalyst the acceleration of the polymerization increases and its depth decreases (figure 2). The temperature drop highly reduces the relation of the maximum velocity to the initial velocity and lengthens the induction period. The observed maximum velocities exceed the sum of the velocities of the separate polymerization of the same monomers with the same initial concentrations. From these data follows that the effect of the acceleration is connected with the initiation acts. This is also indicated by a powerful influence of water and HCl upon the acceleration: as is to be seen from table 3 the acceleration effect is highly inhibited by these additions. The possible causes of a small acceleration at high HCl-concentrations are discussed. Further a partial effect of the reduction of the initial velocity takes place on the introduction of small additions of α-methylstyrene (figure 4). Such a phenomenon is well known in the radical polymerization. With the exhaustion of the quantity of α-methylstyrene the polymerization velocity shall somewhat increase and approach that of pure styrene. It was proved in this paper that the reactivity of the α--methylstyrene molecule in proportion to the carbonium ion

of styrene is considerably higher than that of styrene. Small quantities of the first-mentioned more active component intensively accelerate the styrene polymerization. This effect apparently is of general nature and is connected with a great difference of the activity of the monomers. There are 4 figures, 2 tables, and 3 references, 1 of which is Soviet.

SUBMITTED: October 9, 1957

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SOV/20-122-2-24/42

5(4)

AUTHORS: Ying Shen-K'ang, Pravednikov, A. N., Medvedev, S. S., Member, Academy of Sciences, USSR

TITLE: On the Mechanism of the Cross Linkage of Polymer Chains Under the Action of Gamma Radiation (O mekhanizme sshivaniya polimernykh tsepey pod deystviyem gamma-izlucheniya)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 122, Nr 2, pp 254-257 (USSR)

ABSTRACT: The formation of transverse bonds must be connected with secondary processes in which radicals take part. The velocity of the cross linkage of the chains is constant with respect to time and proportional to the intensity of the radiation. The most simple assumption concerning the mechanism of the cross linkage is the following one: During radiolysis, the transverse bonds are formed by recombination of the polymer radicals to double bonds of the polymer molecules. The steady state with respect to the concentrations of the double bonds and free radicals will be not reached. The recombination of the radicals and the joining-together of the radicals to double bonds play only an unimportant rôle. In order to under-

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On the Mechanism of the Cross Linkage of Polymer Chains Under the Action of Gamma Radiation

stand the mechanism of the processes which lead to the formation of transverse bonds, the radical reactions in the irradiated polymer (especially the reactions in which atomic hydrogen takes part) have to be investigated. This hydrogen atom may either loose its excess energy or react according to one of the following reactions: 1) interaction with an other hydrogen atom: $H + H \longrightarrow H_2$, 2) interaction with free radicals produced during the irradiation

$$\sim CH_2\text{-}\dot{C}H\text{-}CH_2 \sim + H \begin{cases} \nearrow \sim CH_2\text{-}CH_2\text{-}CH_2 \sim \\ \searrow \sim CH_2\text{-}CH{=}CH \sim + H_2 \end{cases}$$

3) interaction with the double bonds: $\sim CH_2\text{-}CH{=}CH \sim + H \longrightarrow$ $\longrightarrow CH_2\text{-}\dot{C}H\text{-}CH_2 \sim$. 4) Detachment of the hydrogen atom from the polymer molecule: $\sim CH_2\text{-}CH_2\text{-}CH_2 \sim + H \longrightarrow \sim CH_2\text{-}\dot{C}H\text{-}CH_2 \sim + H_2$. The velocities of these reactions mainly depend on the probability of the collision of the hydrogen atom with the various

On the Mechanism of the Cross Linkage of Polymer Chains Under the Action of Gamma Radiation

groupings. Below the vitrification temperature T_c, the velocities of the cross linkage of polyethylene and polyvinylchloride do not depend on the temperature. In polymers which contain a sufficiently high number of lateral groupings (bokovaya grupirovka), the "cold" hydrogen atoms will take part in the reactions of cross linkage also below the vitrification temperature. In order to prove this assumption, the authors investigated the influence of the γ-radiation on polymers of the structure $\left(-C_3H_6-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}H_2-\right)_n$.

There are 2 figures, 3 tables, and 2 references, 0 of which is Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy fiziko-khimicheskiy institut im. L. Ya. Karpova
(Physical-Chemical Scientific Research Institute imeni L. Ya. Karpov)

5(3), 5(4)

AUTHORS: Aleksandrova, Yu. A., Huang Yü-li , SOV/20-123-6-20/50
Pravednikov, A. N., Medvedev, S. S Academician

TITLE: Reactions of Oxygen-Containing Radicals of the RO' Type (Reaktsii kislorodsoderzhashchikh radikalov tipa RO')

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 123, Nr 6, pp 1029 - 1032 (USSR)

ABSTRACT: The reactions under review were carried out mainly on model systems in which the RO'-radicals were formed from the decomposition of dialkyl peroxides. The authors found that at the decomposition of ditertiary-butyl-peroxide, dissolved in hydrocarbons, in addition to methane at 195° the resulting amount of acetone is about 12 times that of tertiary butyl alcohol. This is indicative of a higher activation energy than had been found by J. H. T. Brook (Bruk) (Ref 2). Proceeding from scheme (I), (II), (III), nearly all tertiary butoxy radicals are likely decompose under cleavage of the C-C bond as can be assumed from the results obtained. This is, however, in contradiction to the data published on the "thermal-oxidative" destruction of the carbon chain polymers (Ref 4). It

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can be concluded from the results that acetone here is not only formed as a consequence of the reaction :

$(CH_3)_3CO\cdot \xrightarrow{k_1} (CH_3)_2C = O + .CH_3$ (I), but also in consequence of some other reaction the velocity of which considerably depends on temperature. Such a reaction can be that of the RO·-radicals with one another. At low temperatures the concentration of the RO· radicals is low and the reaction proceeds slowly (Ref 2). In order to prove the acceleration of this reaction at increasing temperature or at a considerable increase in concentration of the peroxide, the authors have investigated the decomposition of the di-tertiary-butyl-peroxide in an isopropyl-benzene solution at 12o - 15o° and in the concentration range from 4 up to 16 percentage by weight. Figure 1 shows that the ratio of the concentrations of acetone (a) and tertiary butyl alcohol (b) a/b increases with an increasing concentration of the peroxide. Therefore the reaction order of the formation of these compounds with respect to the peroxide concentration is not equal to 1. According to various computations the authors conclude that the acetone

formation under the above conditions at temperatures of about 200° is largely related with the bimolecular reaction:

$(CH_3)_3CO\cdot + (CH_3)_3CO\cdot \xrightarrow{k_4} (CH_3)_2C = O + CH_3\text{-}O\text{-}C(CH_3)_3$ (IV) and not with the monomolecular decomposition of the RO• radicals. In the case of high-polymers the reaction (IV) must lead to a rapid variation of the distribution regarding the molecular weights. This occurs indeed in the radical stages of the polyethylene oxidation. This variation is accompanied by the occurrence of ether bridges between the macromolecules. There are 4 figures, 1 table, and 5 references, 3 of which are Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy fiziko-khimicheskiy institut im. L. Ya. Karpova (Scientific Physical-Chemical Research Institute imeni L. Ya. Karpov)

SUBMITTED: September 29, 1958

MEDVEDEV, S.S.

PHASE I BOOK EXPLOITATION SOV/5084

International Conference on the Peaceful Uses of Atomic Energy. 2d, Geneva, 1958.

Doklady sovetskikh uchenykh. [t.4] Khimiya radioelementov i radiatsionnykh prevrashcheniy (Reports of Soviet Scientists. v. 4.: Chemistry of Radio-elements and Radiation Transformations) Moscow, Atomizdat, 1959. 323 p. 8,000 copies printed. (Series: Its: Trudy)

Ed. (Title page): A. P. Vinogradov, Academician; Ed.: V. I. Labaznov; Tech. Ed.: Ye. I. Mazel'.

PURPOSE: This collection of articles is intended for scientists and engineers interested in the applications of radioactive materials in science and industry.

COVERAGE: The book contains 26 separate studies concerning various aspects of the chemistry of certain radioactive elements and the processes of radiation effect on matter. These reports discuss present-day methods of reprocessing irradiated nuclear fuel, research in the chemistry of mercury, thorium, uranium, plutonium, and americium, problems related to the sorption and burying of radioactive wastes, the radiolysis of aqueous solutions and of organic compounds, the mechanism of polymer chain grafting, and the effect of radiation on natural and synthetic rubbers. V. N. Prusakov edited the present volume. Most of the reports are accompanied by references. Contributors to individual investigations are mentioned in annotations to the Table of Contents.

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[The following are mentioned as having developed experimental techniques and analysis methods relative to this investigation: Yu. A. Klyachko, L. L. Kunin, and Ye. M. Chistyakova (TsNIIChM - Tsentral'nyy nauchno-issledovatel'skiy institut chernoy metallurgii - Central Scientific Research Institute of Ferrous Metallurgy); N. M. Rostotskaya and K. G. Semenyuk (GEOKhI - Institut geokhimii i analiticheskoy khimii - Institute of Geochemistry and Analytical Chemistry); and V. I. Malyshev (FIAN - Fizicheskiy institut AN SSSR - Institute of Physics AS USSR)]. 16

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Polymerization in emulsions under the action of γ-radiation. Vysokom.soed. 1 no.1:68-72 Ja '59. (MIRA 12:9)

1. Fiziko-khimicheskiy institut im. L.Ya.Karpova.
(Polymerization) (Gamma rays)

ZABOLOTSKAYA, Ye.V.; GANTMAKHER, A.R.; MEDVEDEV, S.S.

Polymerization of styrene with the simultaneous action of a catalyst and light. Vysokom. soed. 1 no.3:460-465 Mr '59.
(MIRA 12:10)

1.Fiziko-khimicheskiy institut im. L. Ya. Karpova.
(Polymerization) (Styrene)

SPIRIN, Yu.L.; GANTMAKHER, A.R.; MEDVEDEV, S.S.

Mechanism of polymerization in the presence of alkali metal organic compounds. Vysokom.soed. 1 no.8:1258-1265 Ag '59. (MIRA 13:2)

1. Fiziko-khimicheskiy institut im. L.Ya.Karpova.
(Polymerization) (Alkali metal compounds)

LYUDVIG, Ye.B.; GANTMAKHER, A.R.; MEDVEDEV, S.S.

Characteristics of the mechanism of cationic polymerization. Part 1: Copolymerization of the systems α-methylstyrene - styrene, isobutylene - styrene and n-butyl vinyl ether - styrene. Vysokom. soed. 1 no.9:1333-1341 S '59. (MIRA 13:3)

1.Fiziko-khimicheskiy institut im. L.Ya. Karpova.
(Styrene) (Ether) (Propene) (Polymerization)

LYUDVIG, Ye. V.; GANTMAKHER, A.R.; MEDVEDEV, S.S.

Characteristics of the mechanism of cationic polymerization. Part 2: Mechanism of the fundamental reactions of cationic polymerization. Vysokom. soed. 1 no.9:1342-1350 S '59. (MIRA 13:3)

1.Fiziko-khimicheskiy institut im. L. Ya. Karpova.
(Polymerization) (Styrene) (Propene)

GANTMAKHER, A.R.; SPIRIN, Yu.L.; [illegible]EDVEDEV, S.S.

Polymerization and copolymerization of fluorinated styrenes.
Vysokom.soed. 1 no.10:1526-1530 O '59. (MIRA 13:3)

1. Fiziko-khimicheskiy institut im.L.Ya.Karpova.
(Styrene) (Polymerization)

5(3)

AUTHORS: Yur'yev, V. M., Pravednikov, A. N., Medvedev, S. S., Academician

SOV/20-124-2-26/71

TITLE: Influence of Side Chains on the Rate of Oxidation of Carbon Chain Polymers (Vliyaniye bokovykh otvetvleniy na skorost' okisleniya karbotsepnykh polimerov)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 2, pp 335-337 (USSR)

ABSTRACT: The principal reactions in the oxidation of hydrocarbons are the following:

$R\cdot + O_2 \longrightarrow ROO\cdot$ (1); $ROO\cdot + RH \longrightarrow ROOH + R\cdot$ (2);

$ROOH \longrightarrow RO\cdot + \cdot OH$ (3); $RO\cdot + RH \longrightarrow ROH + R\cdot$,

$\cdot OH + RH \longrightarrow H_2O + R\cdot$ (4). The rates of all these elementary reactions determine the rate of oxidation. As is known the rate is considerably decreased on the transition from low molecular weight to high molecular weight compounds of analogous structure (Refs 1, 2). This might be explained as follows: The removal of one hydrogen atom from the hydrocarbon atom is accompanied by a

transition of the corresponding link of the molecule from a tetrahedral to a plane configuration. In polymers, links of the polymer chain are displaced. This is bound to increase the activation energy and thus to retard the reaction (as compared with the analogous reactions of low molecular weight compounds). The separation of one hydrogen atom from a side group (methyl-, propyl- and others) is not accompanied by a displacement of the links of the polymer chains and must possess the same activation energy as the corresponding reactions of the low molecular weight compounds. It can therefore be expected that the oxidation of the polymers with comparatively short side chains will take place mainly on the side chains. To control this assumption the authors synthesized polymethylene as well as polymers which contained the methyl and propyl side groups (Ref 4). The experiments concerning the oxidation of these polymers have shown that the introduction of side groups rapidly increases the absorption rate of oxygen (Fig 1,a); at the same time the number of oxygen molecules which are used for the cleavage of the principal chain (Figs 3, 4) increases, i.e. the oxidation really proceeds in the side chains prevalently. At a high oxidation intensity of the polymers which were produced by decomposition

of the diazo compounds, a "sewing up" (zashivaniye) of the polymer results as a consequence of ether bridges between the macro-molecules. A very low molecular fraction appears within the system as well. Possibly, these variations are due to the proceeding of a bimolecular reaction under participation of 2 oxygen containing radicals (Ref 6). Polystyrene is not "sewed up" at an oxidation intensity of up to about 20 ml O_2 per 1 g polymer, since the concentration of the radicals and the oxidation rates, respectively, seem to be too low. There are 4 figures and 6 references, 3 of which are Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy fiziko-khimicheskiy institut im. L. Ya. Karpova (Scientific Physical and Chemical Research Institute imeni L. Ya. Karpov)

SUBMITTED: September 29, 1958

5 (4), 5 (3)

AUTHORS: Yur'yev, V. M., Pravednikov, A. N., Medvedev, S. S., Academician

SOV/20-125-6-36/61

TITLE: The Influence of Oxidation Products on the Kinetics of the Oxidation of Cetane (Vliyaniye produktov okisleniya na kinetiku okisleniya tsetana)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 125, Nr 6, pp 1301-1302 (USSR)

ABSTRACT: The oxidation of cetane takes place at 140° in a closed system with circulating oxygen. Figure 1 shows that, up to a reaction yield of 25-30 %, the reaction develops autocatalytically, after which it decreases rapidly and continues at a nearly constant rate above a reaction yield of 40-50 %. The concentration of peroxide compounds has a maximum at a reaction yield of 25-30 %, after which it also decreases and becomes nearly constant at a reaction yield of 40-50 %. These phenomena are indicative of the fact that, in the course of oxidation, processes occur which reduce the rate of oxidation. As in the case of hydrocarbon oxidation, the system becomes divided into two layers in the course of the process, an upper layer containing hydrocarbons and a

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lower one consisting of oxidation products, products of the lower layer were added to the cetane, which resulted in a reduction of the reaction rate (Fig 3). On the other hand, removal of the lower layer from the reaction vessel caused acceleration of the reaction. This proves that the reduction of reaction rate is caused by the accumulation of products which interrupt the development of the reaction. There are 3 figures.

ASSOCIATION: Nauchno-issledovatel'skiy fiziko-khimicheskiy institut im. L. Ya. Karpova (Scientific Research Institute for Physical Chemistry imeni L. Ya. Karpov)

SUBMITTED: February 11, 1959

5 (2)

AUTHORS: Gantmakher, A. R., Medvedev, S. S., Academician, Lyudvig, Ye. B. SOV/20-127-1-26/65

TITLE: On the Initiation Mechanism of Cationic Polymerization in the Presence of Metal Halides (K voprosu o mekhanizme initsiirovaniya kationnoy polimerizatsii v prisutsvii galogenidov metallov)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 1, pp 100 - 103 (USSR)

ABSTRACT: There are two interpretations concerning the initiation mechanism of carbonium polymerization and of the formation of the primary carbonium ion, respectively: (a) Cationic polymerization cannot proceed in the presence of metal halides without an addition of various co-catalysts. (b) This polymerization is possible under certain conditions without the additions mentioned. The problem of the nature of the co-catalytic additions developed considerably with the progress of investigations. In references 1-3 it was detected for isobutylene polymerization in liquid and in hexane solution that no polymerization takes place without proton-containing additions. Therefrom it results that always proton-containing acids of the type $HB \cdot PX_n$ act as

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initiators of the aforesaid polymerization (HB - co-catalyst PX_n-metal halide). This held in the case of low temperatures and media with a low dielectric constant. The results of isoprene- and styrene polymerization in the presence of $SnCl_4$ obtained by the authors showed, however, that the polymerization mentioned proceeds as well without additions at higher temperature and a higher dielectric constant (Ref 4). This fact concerning halogen alkyls and dichloro-ethane without additions (Refs 7,8,11) was confirmed by references 5,6. The authors of the two last-mentioned papers were, however, of the opinion that the solvent plays here the role of a co-catalyst (see Scheme). The scheme mentioned shows that the breaking of the chain in chloro-ethyl and dichloro-ethane with $TiCl_4$ or $SnCl_4$ as catalysts should not depend on the question as to whether the reaction is carried out in the presence of HCl or without this acid, since the carbonium ion is in either case in the field of one and the same compensating ion. This is in contrast to the authors' results according to which HCl additions reduce the molecular weight of polymers produced by the polymerization in halogen alkylic- and other solvents (Ref 7). Only the

molecules bound to the catalysts are effective. From these and other results (Refs 8-11) the authors drew the conclusion that the cationic polymerization may proceed under the direct effect of aprotic acids in halogen alkylic solvents without the participation of specific co-catalysts. This holds also for water (Refs 5,6). In reference 12 it is, however, not denied that both (a) and (b) polymerization methods are possible. The initiation reaction in the monomer - catalyst system proceeds apparently by way of the formation of a π-complex of the catalyst with the monomer. The initiation reaction is caused by an interaction between this complex and the monomer (Refs 8,13; analogy in reference 14). Thus, complex formation effects (Refs 11, 15) are inhibited by additions of H_2O and HCl (Ref 11) which form themselves stable complexes with $SnCl_4$. α-methyl styrene forms complexes with $SnCl_4$ better than the styrene used in references 1-3. It is rather probable that the co-catalysts form in non-polar solvents not only complexes with the catalyst, but also favor the formation of an ion couple by the solvation of the complex. The additions themselves may play this role as

well as their complexes with the catalyst. Thus, polymerization without co-catalyst is in several systems one of the special cases of the complex nature of the initiation process. There are 16 references, 9 of which are Soviet.

SUBMITTED: April 20, 1959

5(3).

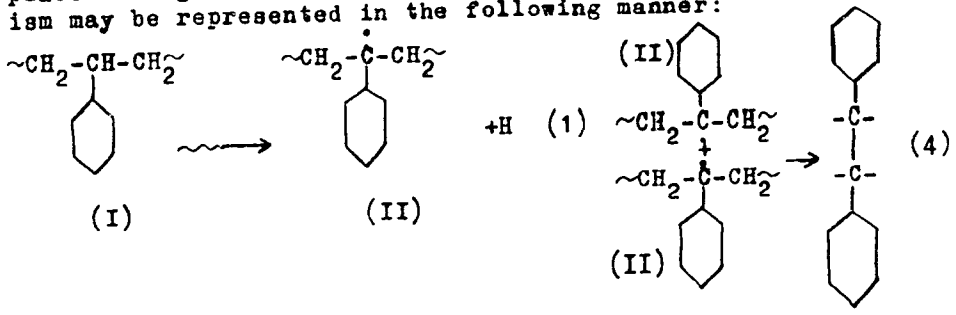
SOV/2o-127-3-33/71

AUTHORS: In Shen-kan, Pravednikov, A. N., Medvedev, S. S., Academician

TITLE: The Mechanism of the Screening Effect of Benzene Rings in the Hydrolysis of Polystyrene

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 3, pp 595-598 (USSR)

ABSTRACT: Polystyrene has a considerable radiation stability compared to polyethylene and compounds containing nc phenyl group. For cross-linking an exceedingly high energy is necessary. In this connection, the reaction is investigated which takes place during irradiation on polystyrene. The reaction mechanism may be represented in the following manner:



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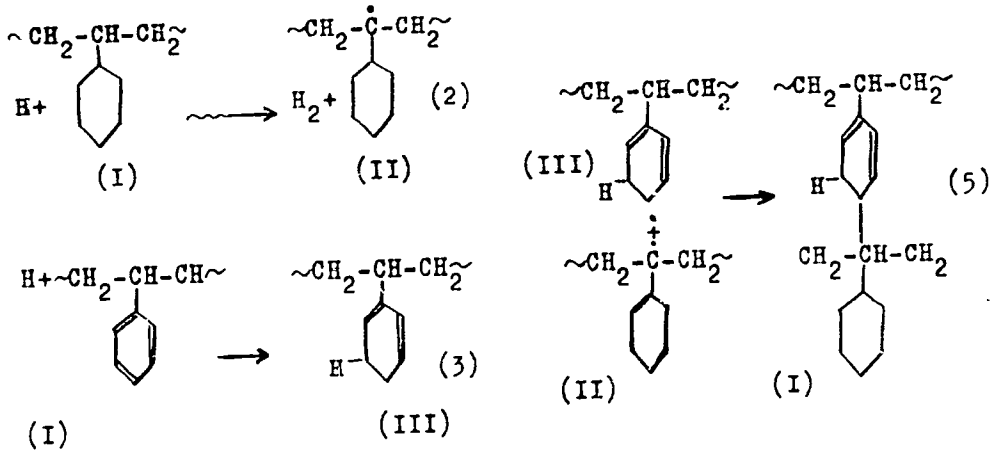
SOV/20-127-3-33/71

The Mechanism of the Screening Effect of Benzene Rings in the Hydrolysis of Polystyrene



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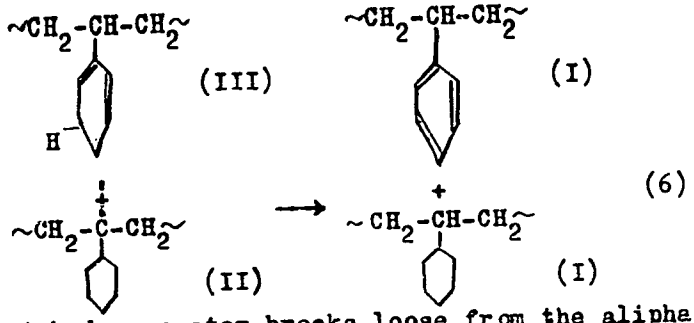
The Mechanism of the Screening Effect of Benzene Rings in the Hydrolysis of Polystyrene



A hydrogen atom breaks loose from the aliphatic chain; it may react with the styrene by a further separation of a hydrogen atom (2), or it may link up to the benzene ring by forming a free cyclohexadienyl radical (3). The latter reaction develops very rapidly. If, further, (II) reacts with (II), a "transversal compound" may be formed (4), or (II) reacts with (III), in which case this reaction may lead to the "transversal compound" (5), and with further disproportionation (6) to the re-formation of the benzene ring. Experiments

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SOV/20-127-3-33/71

The Mechanism of the Screening Effect of Benzene Rings in the Hydrolysis of Polystyrene

carried out with deuterium-substituted toluene proved the mechanism mentioned in (6). Data hereon (deuteron content in the compounds obtained and energy used for transition of a D-atom into the benzene ring)are given in table 1. The high stability of polystyrene to cross-linking may be explained by the disproportionation of the primary radicals with the cyclohexadiene radical. There is 1 table and 7 English references.

ASSOCIATION: Nauchno-issledovatel'skiy fiziko-khimicheskiy institut im. L. Ya. Karpova
(Scientific Research Institute for Physical Chemistry imeni L. Ya. Karpov)

SUBMITTED: April 17, 1959

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~~5 (4)~~ 5.3830 (A), 5.3831 66433

AUTHORS: Spirin, Yu. L., Gantmakher, A. R., Medvedev, S. S., Academician SOV/20-128-6-38/63

TITLE: The Copolymerization of Parachlorostyrene With α-Methylstyrene and Styrene Under the Influence of Alkaline Catalysts

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 6, pp 1232 - 1233 (USSR)

ABSTRACT: An investigation is made of the reactivity of chlorine-containing monomers under the influence of lithium-organic and sodium-organic catalysts in different media. The polymerization took place in a vacuum, to exclude the effects of air and humidity. Previous experiments with monomers containing a relatively mobile chlorine atom (chlorovinyl, chloroprene) showed that the chlorine atom quickly reacts with lithiumethyl and that no polymerization takes place even at low temperatures. The chlorine atom of parachlorostyrene is, however, less mobile, and thus it is possible to carry out the polymerization. Table 1 gives the results of the experiments. Lithiumethyl, sodium triphenylmethyl, α-sodium naphthalene and γ-radiation were used as catalysts; the solvents were benzene, ether, triethylamine, and tetrahydrofuran. The composition of the copolymers strongly depended on the kind

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The Copolymerization of Parachlorostyrene With α-Methyl- SOV/20-128-6-38/63
styrene and Styrene Under the Influence of Alkaline Catalysts

of catalyst and medium. In the case of hydrocarbons the radical polymerization is predominant in the polymerization with lithiumethyl. The same radical polymerization also prevails under the effect of γ-radiation. In the case of triethylamine the polymerization according to the anion mechanism is most frquent, while when lithiumethyl is used in ether radical mechanism and anion mechanism are found side by side. The constants of anionic copolymerization calculated for styrene ($\alpha = 0.1 \pm 0.1$) and parachlorostyrene ($\beta = 6.5 \pm 0.1$) show that the introduction of the chlorine atom into styrene increases the activity of the monomer for anionic polymerization. There are 1 table and 2 references, 1 of which is Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy fiziko-khimicheskiy institut im. L. Ya. Karpova (Scientific Research Institute of Physical Chemistry imeni L. Ya. Karpov)

SUBMITTED: July 6, 1959

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MEDVEDEV, S. S.

PHASE I BOOK EXPLOITATION SOV/4984

International symposium on macromolecular chemistry. Moscow, 1960.

Mezhdunarodnyy simpozium po makromolekulyarnoy khimii SSSR, Moskva, 14-18 iyunya 1960 g.; doklady i avtoreferaty. Sektsiya III. (International Symposium on Macromolecular Chemistry Held in Moscow, June 14-18, 1960; Papers and Summaries) Section III. [Moscow, Izd-vo AN SSSR, 1960] 469 p. 55,000 copies printed.

Tech. Ed.: P. S. Kashina.

Sponsoring Agency: The International Union of Pure and Applied Chemistry. Commission on Macromolecular Chemistry.

PURPOSE: This book is intended for chemists interested in polymerization reactions and the synthesis of high molecular compounds.

COVERAGE: This is Section III of a multivolume work containing papers on macromolecular chemistry. The articles in general deal with the kinetics of polymerization reactions, the synthesis of special-purpose polymers, e.g., ion exchange resins, semiconductor materials, etc., methods of catalyzing polymerization reactions, properties and chemical interactions of high molecular materials, and the effects of various factors on polymerization and the degradation of high molecular compounds. No personalities are mentioned. References given follow the articles.

Yur'yev, V. M., A. N. Pravednikov, and S. S. Medvedev (USSR). The Effect of Formic Acid and Formates on the Oxidation of Hydrocarbons and Hydrocarbon Polymers 364

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MEDVEDEV, S.S.

PHASE I BOOK EXPLOITATION SOV/4983

International symposium on macromolecular chemistry. Moscow, 1960.

Mezhdunarodnyy simpozium po makromolekulyarnoy khimii, SSSR, Moskva, 14-18 iyunya 1960 g; doklady i avtoreferaty. Sektsiya II. (International Symposium on Macromolecular Chemistry Held in Moscow, June 14-18; Papers and Summaries) Section II. [Moscow, Izd-vo AN SSSR, 1960] 559 p. 5,500 copies printed.

Sponsoring Agency: The International Union of Pure and Applied Chemistry, Commission on Macromolecular Chemistry

Tech. Ed.: T.A. Prusakova.

PURPOSE: This book is intended for chemists interested in polymerization reactions and the synthesis of high-molecular compounds.

COVERAGE: This is Section II of a multivolume work containing papers on macromolecular chemistry. The papers in this volume treat mainly the kinetics of various polymerization reactions initiated by different catalysts or induced by radiation. Among the research techniques discussed are electron paramagnetic resonance spectroscopy and light-scattering interpolation. There are summaries in English, French and Russian. No personalities are mentioned. References follow each article.

Bagdasar'yan, Kh.S., and Z.A. Sinitsina (USSR). Inhibition of Polymerization by Aromatic Compounds 22

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Ržásal, Z., and A. Kazda (Czechoslovakia). On the Role of Nonpolar Compounds in the Cationic Polymerization of Isobutylene 272

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BEREZHNOY, G.D.; KHOMIKOVSKIY, P.M.; MEDVEDEV, S.S.

Kinetics of the emulsion polymerization of styrene. Vysokom. soed. 2 no.1:141-152 Ja '60. (MIRA 13:5)

1. Moskovskiy institut tonkoy khimicheskoy tekhnologii i Fiziko-khimicheskiy institut im. L.Ya.Karpova.
(Styrene) (Polymerization)

81612

S/190/60/002/02/11/011
B004/B061

5.3831

AUTHORS: Spirin, Yu. L., Gantmakher, A. R., Medvedev, S. S.

TITLE: Electron Absorption Spectra of Carbanions in the Polymerization of Styrene in the Presence of Organometallic Compounds

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 2, pp. 310-312

TEXT: The authors proceed from the data published in Refs. 1-4, according to which the composition of copolymers changes when, instead of organosodium, organolithium compounds are used as catalysts, and the polymerization occurs in hydrocarbons instead of in amines and ethers. The polymerization is accelerated by the conversion of LiR to NaR and the substitution of amines, ether, or tetrahydrofurane for hydrocarbon. The authors infer from this that the structure of the carbanion components of the catalysts for LiR and NaR differ not only in hydrocarbons but also in polar solvents. This was checked by examining the

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Electron Absorption Spectra of Carbanions in the Polymerization of Styrene in the Presence of Organometallic Compounds

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absorption spectra in the near ultraviolet range. The spectra of carbanions formed by polymerization of styrene in the presence of LiR or NaR in different media were taken with an СФ-4 (SF-4) spectrophotometer according to I. V. Astaf'yev's method (Ref. 6), excluding dampness and oxygen. Fig. 1 shows the dependence of the optical density on the wavelength for lithium polystyrene in different media, Fig. 2, the same for sodium polystyrene, and Table 1 gives the absorption maxima. The results are: The absorption maximum is shifted to longer waves (from 330 mμ to 395 mμ) by the use of organosodium compounds. This confirms the strengthening of the carbanion character in NaR as opposed to LiR. The solvent (toluene, toluene + triethylamine, toluene + tetrahydrofurane) has no effect on the position of the absorption bands, and only changes the intensity of absorption. There are 2 figures, 1 table, and 6 references: 3 Soviet and 3 US.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

81612

Electron Absorption Spectra of Carbanions in the Polymerization of Styrene in the Presence of Organometallic Compounds

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B004/B061

SUBMITTED: December 4, 1959

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83704
S/190/60/002/006/009/012
B015/B064

15.8101 also 2209

AUTHORS: Medvedev, S. S., Abkin, A. D., Khomikovskiy, P. M., Gerasimov, G. N., Gromov, V. F., Chikin, Yu. A., Tsingister, V. A., Auer, A. L., Yakovleva, M. K., Mezhirova, L. P., Matveyeva, A. V., Bezzubik Z. G.

TITLE: Polymerization of Ethylene Under the Influence of γ-Radiation

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 6, pp. 904-915

TEXT: The radiation-chemical polymerization of ethylene in the gaseous phase and in organic substances was investigated at different pressure and radiation dose as well as some properties of the polymers formed Co^{60} γ-radiation sources of the institut im. Karpova (Institute imeni Karpov) (1400, 1800, and 20000 gram equiv. Ra) and pressures of 50-300 atm, radiation dose of 17 to 165 r/sec, and 25°C (some experiments were made at 50°C) were the conditions. The experiments were carried out in a corresponding device (Fig. 1). The ethylene used was mass-

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spectroscopically analyzed by M. V. Tikhomirov and M. V. Gur'yev. The molecular weight of the polyethylene obtained was determined by the method of light scattering by I. G. Sobcleva and N. V. Mekletsova; particular data on this will be given in a separate paper. The experiments of polymerization in heptane, cyclohexane, methanol, and acetone (50 atm, 25°C, ~100 r/sec) showed (Table 1) that reaction proceeds ten times more rapidly than in the gaseous phase. The polymers formed have a molecular weight of 20000-40000. Polymers of the structure $Cl_3C(C_2H_4)_2Cl$ (60%) and $Cl_3C(C_2H_4)_3Cl$ (20%) form in good yield in carbon tetrachloride. Polymerization in the gaseous phase was investigated at constant pressure (100-300 atm, 72 r/sec) and decreasing pressure (100 and 150 atm, 17-165 r/sec, 25° and 50°C). The polymer yield increases rapidly if experiments are made in the presence of polyethylene (Table 2). To begin with, the polymerization rate increases with time and reaches then a constant value. The mean molecular weight and the characteristic viscosity of the polymers increases with proceeding transformation (Table 3). The mean reaction rate amounts to 16.9 g/l.hour at 300 atm, 25°C, a duration of 24 hours and radiation dose of 72 r/sec, and the maximum rate

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Polymerization of Ethylene Under the Influence of γ-Radiation

20.5 g/l.hour (Table 4). The mean molecular weight and viscosity of polyethylene (Table 5) rise with pressure (i.e. the ethylene concentration). The maximum rate of polymerization increases somewhat with the radiation dose with a proportionality factor of 0.3, while the radiation-chemical yield decreases with an increase in the radiation dose with a factor of 0.7. The molecular weight of polyethylene increases with a reduction of the radiation dose with a factor of 0.7. The molecular weight of polyethylene increases with decreasing radiation dose (Table 6). A temperature increase from 25°C to 50°C at constant ethylene concentration (330 g/l) causes a lesser increase in the polymerization rate and the molecular weight (Table 7). Investigations carried out by Yu. M. Malinskiy and B. I. Everev in the laboratory of radiochemistry of the authors' institute showed that the polyethylene obtained has a higher density (0.945-0.975 g/cm^3) and degree of crystallization than high-pressure polyethylene, differs, however, only slightly from the latter with respect to the tensile strength. In conclusion, the authors thank A. Kh. Breger, V. B. Osipov, and V. A. Gol'din for assisting in carrying out the experiments with the gamma emitters. There are 8 figures, 7 tables, and 11 references: 5 Soviet, 4 US, 1 British, and 1 Belgian.

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Polymerization of Ethylene Under the Influence of γ -Radiation

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B015/B064

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: February 24, 1960

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Card 4/4

S/190/60/002/007/012/017
B020/B052

11,2211

AUTHORS: Spirin, Yu. L., Polyakov, D. K., Gantmakher, A. R., Medvadev, S. S.

TITLE: Polymerization and Copolymerization of Isoprene Initiated by Ethyl Lithium

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 7, pp. 1082-1092

√c

TEXT: In a previous paper it has been shown (Ref. 1) that the polymerization mechanism of styrene in the presence of ethyl lithium changes considerably with the transition from a hydrocarbon solvent to a triethylamine toluene mixture. Here, the polymerization and copolymerization laws of isoprene and styrene by ethyl lithium are investigated under various conditions. Ethyl lithium was synthesized by reaction of metallic lithium and ethyl chloride in benzene (Ref. 2). After recrystallization it was solved in toluene, vacuum-filtered and filled into ampoules. From them, the solution was filled into the device shown in Fig. 1. The polymerization was carried out in the dilatometer shown in Fig. 2. The polymers

were precipitated from the obtained solutions by methanol. During the isolation of polyisoprene, the antioxidant Неозон-А (Neozone-D) was added to methanol. The polymers were vacuum-dried, and the viscosity of polystyrene in benzene (Ref. 1), and that of polyisoprene in toluene were determined at 30°. The composition of the copolymers was IR-spectrographically and refractometrically determined from their hydrogen and carbon contents on the basis of the supposition that the intrinsic viscosity is an additive quantity. The difference in the results obtained by various methods, was not more than ±2.5%. The dependence of the polymerization rate of isoprene on the concentration of the monomer in toluene, ethyl lithium in toluene, triethyl amine and the catalyst in a toluene - triethyl amine mixture, is graphically presented in Fig. 3. It is shown that the polymerization rate is proportional to the monomer concentration. In the toluene - amine mixture, the polymerization rate is proportional to the concentration of the catalyst. However, the dependence of the polymerization rate in hydrocarbons in connection with the lithium polyisoprene association, on the concentration of the catalyst, is more complicated. Fig. 4 shows the kinetic curves of the isoprene and styrene polymerization with 0.003 mole/l of ethyl lithium solution in toluene, and in a toluene -

amine mixture. The temperature dependence of the polymerization rate of isoprene in toluene and a toluene - amine mixture, is shown in Figs. 5 and 6. Table 1 gives the activation energies and rate constants during the increase of the chains in the isoprene and styrene polymerizations. For comparison, the same quantities are given as to radical polymerization. E = 14.3 kcal/mole, $k_{30^\circ} = 0.5$ in the polymerization of isoprene in toluene, and in the amine - toluene mixture: E = 9.2 kcal/mole, and $k_{30^\circ} = 0.03$. The dependence of log $[\eta]$ on log M for polyisoprene in toluene, and toluene with a triethylamine addition, are shown in Fig. 7. Table 2 gives the composition of isoprene styrene copolymers in various solvents at 27°C; the kinetic curves of the system under different conditions are given in Fig. 8. The constants of the copolymerization of isoprene and styrene in toluene were found to be $r_1 = 9.5$, $r_2 = 0.25$; in a toluene - amine mixture $r_1 = 1$, $r_2 = 0.8$. On the basis of the results obtained, a polymerization mechanism was suggested for vinyl and diene-monomers in the presence of ethyl lithium under various conditions. There are 8 figures, 2 tables, and 11 references: 6 Soviet and 5 US.

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Polymerization and Copolymerization of Isoprene Initiated by Ethyl Lithium

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ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: March 17, 1960

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S/190/60/002/008/009/017
B004/B054

AUTHORS: Zabolotskaya, Ye. V., Gantmakher, A. R., Medvedev, S. S.

TITLE: Polymerization of Styrene Under the Action of Complex Catalysts

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 8, pp. 1213-1220

TEXT: The authors attempted to determine the mechanism of polymerization of styrene by combined catalysts of $TiCl_3$ and triisobutyl- or triethyl aluminum. Dosing of aluminum alkyl and $TiCl_3$ was conducted in vacuo by means of the glass vessel shown in Fig. 1. Polymerization was performed in the apparatus of Fig. 2. Vessel 1 contained a ball with aluminum alkyl. The apparatus was evacuated to 10^{-3} mm Hg for 18 hours. In a nitrogen flow, $TiCl_3$ was then filled into the dilatometer 2, and the styrene dissolved in benzene was filled into vessel 3. The content of 3 was poured into 1, the ball with the aluminum alkyl broken, and the whole filled into the dilatometer 2. The dilatometer was melted off the vacuum apparatus at 250-300 mm Hg,

and polymerization was performed in a thermostat at 75°C. The following results were obtained: 1) There is a proportionality between the polymerization rate w (moles/l·min) and the $TiCl_3$ concentration: for 0.0228 moles/l of $TiCl_3$, $w \cdot 10^2 = 0.186$; for 0.1430 moles/l of $TiCl_3$, $w \cdot 10^2 = 0.635$. 2) w is a linear function of styrene concentration: for 0.650 moles/l of styrene, $w \cdot 10^2 = 0.060$; for 3.74 moles/l of styrene, $w \cdot 10^2 = 0.379$. 3) The aluminum alkyl concentration (between 0.01 and 0.06 moles/l) and the ratio between $TiCl_3$ and aluminum alkyl do not affect the polymerization rate. 4) A study of the temperature dependence of the polymerization rate showed: at 84°C, $w \cdot 10^2 = 0.281$; at 63.5°C, $w \cdot 10^2 = 0.083$. 5) When calculating $w' = w \cdot 10^3/[TiCl_3][\text{styrene}]$, log w' is a linear function of 1/T. The activation energy was found to be 11.0 kcal/mole. 6) 60-70% of the polymer obtained had a molecular weight of 1,000,000 - 1,500,000. The molecular weight did not depend on the monomer concentration. These data indicate a mechanism of polymerization similar to the polymerization of ethylene and propylene: $M_n^* + M \rightarrow M_n + M^*$. The authors thank Z. V. Zvonkova

Polymerization of Styrene Under the Action of Complex Catalysts

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and N. S. Ivanova for determining the modification of α-$TiCl_3$, and N. T. Makletsova for determining the molecular weight of the polymers. There are 8 figures, 6 tables, and 15 references: 2 Soviet, 6 US, 1 French, 3 German, and 3 Italian.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physicochemical Institute imeni L. Ya. Karpov)

SUBMITTED: March 28, 1960

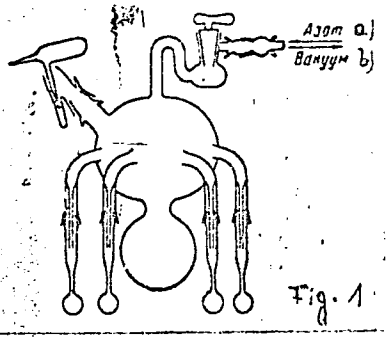

Fig. 1

Legend to Fig. 1: Vessel for dosing the aluminum alkyl a) nitrogen, b) vacuum.

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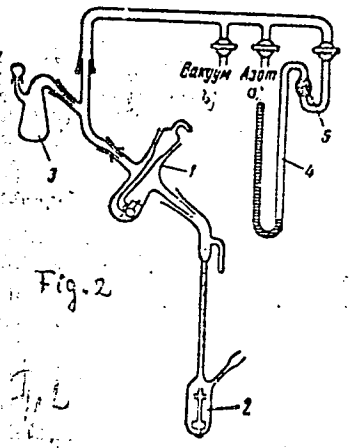

Fig. 2

Legend to Fig. 2: Device for filling the dilatometer a) nitrogen, b) vacuum.

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B004/B054

15.8101 2209, 1103

AUTHORS: Soboleva, I. G. (Deceased), Makletsova, N. V., Medvedev, S. S.

TITLE: Structure of the Molecular Chain of Polyethylene Obtained Under the Action of γ-Radiation

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 8, pp. 1234-1238

TEXT: The present paper gives the results of investigation of the molecular-chain structure of polyethylene polymerized in the gaseous phase by gamma radiation at 25°C. The effect of some admixtures was also studied. Further, the authors calculated the molecular weight (nephelometrically), the intrinsic viscosity of the polymer dissolved in octane, and the root mean square of the distance h between the chain ends by the equation of Flory $[\eta] = \Phi(h^2)^{1/2}/M$, where $[\eta]$ = intrinsic viscosity, Φ = Flory constant, and M = molecular weight. The results are summarized in the following tables: Table 2, effect of admixtures on the average molecular weight of poly-

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Obtained Under the Action of γ-Radiation B004/B054

ethylene

Intensity of radiation, roentgens/sec	Duration of polymerization, h	Pressure, atm	Admixture	Percent by weight of admixture in the mixture	Molecular weight $M \cdot 10^{-3}$
81	36	85.5	-	0	260
81	36	87.6	hydrogen	0.440	80
81	36	87.0	ditto	0.158	80
81	36	87.0	ditto	0.037	100
81	36	87.0	ditto	0.018	60
82	12	100.0	heptane	19.5	60
27	12	100.0	ditto	19.7	40
27	24	100.0	ditto	9.5	66

Table 3, Dependence of the average molecular weight of polyethylene on the initial pressure of ethylene (intensity of radiation 81 roentgens/sec, duration 36 h, temperature 25°C)

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Structure of the Molecular Chain of Polyethylene Obtained Under the Action of γ-Radiation

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Initial pressure, atm	Yield in polymer, %	$M \cdot 10^{-3}$	Initial pressure, atm	Yield in polymer, %	$M \cdot 10^{-3}$
59.6	8.9	50	87.5	21.0	150
65.0	12.4	60	100.0	44.0	320
70.0	18.2	110	100.0	47.0	insoluble

Table 4, Dependence of the mean molecular weight and the intrinsic viscosity on temperature, intensity, and radiation dose:

Temperature, °C	Initial pressure, atm	Dose, 10^{-6} roentgens	Yield %	$M \cdot 10^{-3}$	[η] 100 ml/g in octane 95°C	[η] 100 ml/g in xylene 105°C	h, A in octane 95°C	h, A in xylene 105°C
Intensity 17 roentgens/sec								
25	100	1.47	11.3	130	0.96	-	400	-
25	100	2.26	20.0	200	1.18	-	480	-
25	150	0.73	7.2	330	1.45	1.80	600	650
50	174	0.73	4.7	435	-	1.25	-	640

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Structure of the Molecular Chain of Polyethylene Obtained Under the Action of γ-Radiation

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Table 4 continued:

		Intensity 27 roentgens/sec							
25	100	2.32	13.2	125	0.86	-	370	-	
25	100	3.40	21.6	250	1.32	-	540	-	
25	100	3.90	24.2	490	-	1.95	-	780	
25	150	1.18	11.4	250	-	1.50	-	560	
50	178	1.18	6.1	540	-	1.30	-	700	
		Intensity 33 roentgens/sec							
25	100	1.43	5.7	50	0.65	0.70	225	-	
25	100	2.85	14.9	150	0.77	-	380	-	
25	150	1.43	12.4	280	-	1.55	-	600	
50	176	1.43	8.6	800	-	1.33	-	800	
		Intensity 72 roentgens/sec							
25	100	6.23	22.8	190	0.96	-	450	-	
25	100	9.35	44.0	320	-	1.9	-	660	
25	150	3.12	15.6	260	1.25	1.78	510	600	
25	200	3.12	17.1	280	1.15	1.66	540	600	

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Table 4 continued:

		Intensity 82 roentgens/sec						
25	100	3.54	10.5	56	0.43	-	225	-
25	150	3.54	14.6	125	0.90	-	375	-
50	176	3.54	10.4	230	0.66	0.71	380	430

The following conclusions are drawn: 1) The macromolecular chain of polyethylene shows only slight ramification which only slightly changes in the investigated range of intensity and radiation dose and ethylene concentration. 2) At a temperature increase to 50°C, the molecular weight rises and ramification increases. There are 3 figures, 4 tables, and 7 references: 4 Soviet, 2 US, and 1 Belgian.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova
(Physicochemical Institute imeni L. Ya. Karpov)

SUBMITTED: March 31, 1960

S/190/60/002/009/012/019
B004/B060

AUTHORS: Lanovskaya, L. M., Gantmakher, A. R., Medvedev, S. S.

TITLE: Polymerization of Ethylene by Means of the Combined Catalyst α-$TiCl_3$ - AlR_3 in the Presence of Various Monomers.
I. The Effect of Various Monomers on the Polymerization of Ethylene

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 9, pp. 1391-1397

TEXT: The authors wanted to study the interaction of various unsaturated compounds with the combined catalyst, and its effect on the polymerization of ethylene under conditions at which these compounds still polymerize at a negligibly low rate. The authors describe the purification of the reagents, the reaction vessel (Fig. 2) with magnetic stirrer and

thermostat, and a device (Fig. 1) which served for introducing the octane solvent and the $(i\text{-}C_4H_9)_3Al$ into the reaction vessel. The measurements were made at a constant ethylene pressure of 200 torr by the method developed by A. I. Gel'bshteyn and M. I. Temkin (Ref. 8). The experimental procedure was worked out by Gritsenko and Lanovskaya. α-methyl styrene, isoprene, butadiene, and isobutylene were used as admixtures. In the first series of experiments (Table 1, Fig. 3), the monomer was filled into the reaction vessel before introducing the ethylene. In the second series of experiments (Tables 1,2, Figs. 4-6), the ethylene was first polymerized during two hours, the monomer was then added, and polymerization was carried on for five more hours. In the experiments specified in Table 1, the authors used $TiCl_3$ which was obtained from $TiCl_4$ by reduction by means of antimony. Table 2 specifies

Polymerization of Ethylene by Means of the Combined Catalyst α-$TiCl_3$ - AlR_3 in the Presence of Various Monomers. I. The Effect of Various Monomers on the Polymerization of Ethylene

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the experiments in which $TiCl_3$ was produced by the reduction of $TiCl_4$ by means of titanium metal. Experiments revealed that the polymerization rate of ethylene is retarded in the presence of one of the monomer compounds mentioned. The molecular weight of the resulting polyethylene is, however, not influenced thereby. As to their reaction-retarding effect, the various monomer compounds are mentioned in the order butadiene, isoprene > styrene > isobutylene > α-methyl styrene. Diene hydrocarbons, thus, have the greatest retarding effect. The addition of monomers prior to or after the beginning of polymerization bears no influence on this effect. The authors mention a discussion by A. R. Gantmakher on a lecture by A. A. Korotkov at the International Symposium in Prague, 1957. There are 6 figures, 2 tables, and 8 references: 2 Soviet, 4 US, and 2 German.

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Polymerization of Ethylene by Means of the Combined Catalyst α-$TiCl_3$ - AlR_3 in the Presence of Various Monomers. I. The Effect of Various Monomers on the Polymerization of Ethylene

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B004/B060

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ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: April 11, 1960

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S/190/60/002/011/010/027
B004/B060

15.8101

AUTHORS: Lanovskaya, L. M., Gantmakher, A. R., Medvedev, S. S.

TITLE: Polymerization of Ethylene by Means of Combined α-$TiCl_3$-AlR_3 Catalyst in the Presence of Various Monomers II. Some Problems Concerning the Polymerization Mechanism in the Presence of Combined Catalysts

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol 2, No 11, pp. 1655 - 1658

TEXT: This is a discussion of the results obtained by the authors in Ref 1 concerning the effect of various monomers on the polymerization of ethylene by α-$TiCl_3$-AlR_3 catalysts. The authors' experiments revealed that additions of isobutylene, styrene, isoprene, or butadiene reduce the polymerization rate of ethylene, complexes of these monomers being formed on the catalyst surface. The ability to form complexes is reduced in the series butadiene > isoprene > styrene > isobutylene > α-methyl styrene. This succession is analogous to the series obtained by other researchers for

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Polymerization of Ethylene by Means of Combined α-$TiCl_3$-AlR_3 Catalyst in the Presence of Various Monomers. II. Some Problems Concerning the Polymerization Mechanism in the Presence of Combined Catalysts

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compounds of platinum, silver, and other metals. The authors base on their experimental results to conclude that the monomers react with the titanium component of the catalyst. A reaction with the aluminum component, which is a Lewis acid, would yield another series of activities. The following reaction scheme is given:

$$TiCl_3 \cdot Al\begin{matrix}R\\R\\M_nR\end{matrix} + M \underset{k_2}{\overset{k_1}{\rightleftharpoons}} M \cdot TiCl_3 \cdot Al\begin{matrix}R\\R\\M_nR\end{matrix} \quad (1) \qquad M \cdot TiCl_3 \cdot Al\begin{matrix}R\\R\\M_nR\end{matrix} \xrightarrow{k_3} TiCl_3 \cdot Al\begin{matrix}R\\R\\M_{n+1}R\end{matrix} \quad (2).$$

Polymerization by combined catalysts thus does not have a typical anionic course, but is a more complicated process. This has some resemblance with polymerization in the presence of lithium alkyls, but differs from it by specific properties which depend on the structure of the combined catalyst. The authors mention A. A. Babushkin, L. A. Gribov, and A. D. Gel'man. There are 14 references: 5 Soviet, 4 US, 3 British, 1 French, and 1 German.

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Polymerization of Ethylene by Means of Combined α-$TiCl_3$-AlR_3 Catalyst in the Presence of Various Monomers. II. Some Problems Concerning the Polymerization Mechanism in the Presence of Combined Catalysts

S/190/60/002/011/010/027
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ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: May 5, 1960

Card 3/3

MEDVEDEV, S. S.

To be submitted for the International Symposium on Macromolecular Chemistry, Montreal, Canada, 27 Jul -1 Aug 1961.

USSR

BIRSHTEIN, T. M., Institute of High Molecular Chemistry, Academy of Sciences USSR, Leningrad, jointly with KRIGBAUM, W. R., and KANEKO, M., Duke University, Durham, N.C. - "Elasticity of cube lattice chain networks" (Group 2)

DOGADKIN, Boris A., and DONTSOV, A. A., Moscow Institute of Fine Chemical Technology imeni M. V. Lomonosov - "Interaction of polyethylene with sulphur" (Groups 4-5)

KARGIN, Valentin A., Head, Laboratory of Colloidal Chemistry, Scientific Research Physico-Chemical Institute imeni L. Ya. Karpov, Moscow - "The formation of big crystal structures in polymers and their properties" (Group 2. Invited lecture)

KRENTSEL', B. A., TOPCHIYEV, A. V., and BAKALO, L. A., Institute of Petroleum, Academy of Sciences USSR, Moscow - "Polymerization of some epoxy compounds" (Group 3-B) (Yu. 4)

MEDVEDEV, Sergey S., SPIRIN, YU. A., AREST-YAKUBOVICH, A. A., POLYAKOV, D. K., and GANTMAKHER, A. R., Scientific Research Physico-Chemical Institute imeni L. Ya. Karpov, Moscow - "Polymerization catalyzed by lithium and lithium alkyl" (In German) Group 3-B)

NAMETKIN, N. S., TOPCHIYEV, A. V., and POLAK, L. S., Institute of Petrochemical Synthesis, Academy of Sciences USSR, Moscow - "On the catalytic polymerization and radiochemistry of allylsilans" (Group 3-A)

PIOTROVSKIY, K. B., All-Union Scientific Research Institute of Synthetic Rubber imeni S. V. Lebedev, Leningrad - "Temperature effect on polymer structure in diene polymerization by alkali metals" (Group 3-B)

PODDUBNYY, I. Ya., and ERENBURG, Ye. G., All-Union Scientific Research Institute of Synthetic Rubber, Leningrad - "Study of branching in regular isoprene polymers" (Group 1)

PODDUBNYI, I. Ya. MOSEVITSKIY, M. I. RABINERZON, M. A., and PERVUKHOV, A. M. All-Union Scientific Research Institute of Synthetic Rubber imeni S. V. Lebedev, Leningrad - "Nature of molecular-weight distribution and properties of styrene-butadiene rubbers depending on polymerization conditions" (Group 3-A)

PRAVEDNIKOV, A. N., TELESHOV, Ye. N., YING, Sha-k'ang, and MEDVEDEV, S. S., Scientific Research Physico-Chemical Institute ~~imeni L.~~ Ya. Karpov, Moscow - "Investigation of the mechanism of radiolysis of polymers containing quaternary atoms of carbon" (Group 4-5) (Yu. 4)

TSVETKOV, Viktor N., Institute of High Molecular Compounds of the Academy of Sciences USSR, Leningrad - "Stereo-regularity and optical anisotropy of macromolecules" (Group not specified)

USMANOV, Khamdam U., and SUSHKEVICH, T. I., Academy of Sciences UzSSR, Tashkent, Uzbekistan - "The investigation of the cotton cellulose polydispersity according to the molecular weight" (Group not specified)

YENIKOLOPYAN, N. S., Institute of Chemical Physics of the Academy of Sciences USSR, Moscow - "On the kinetics of formaldehyde polymerization and polyformaldehyde degradation" (Group 3-B)

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B101/B215

15,8115

AUTHORS: Gantmakher, A. R., Medvedev, S. S., Abkin, A. D.

TITLE: Low-temperature polymerization of ethylene tetrafluoride in liquid phase by the action of gamma radiation

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 2, 1961, 320

TEXT: In this letter to the editor the authors state that they were the first to examine the liquid phase polymerization of ethylene tetrafluoride under the action of gamma radiation. The polymerization was conducted in sealed glass phials in the absence of oxygen, at -55°C and 10 roentgen/sec. Under these conditions, the reaction took place at a high rate and was accompanied by the formation of a solid polymer. Afer one hour, the yield of polyethylene tetrafluoride was 35%. It was increased up to 95% by a radiation of 6 hr. The studies were continued by Ye. F. Volkova, A. V. Fokin, V. M. Belikov (Tezisy dokladov na II Vsesoyuznom soveshchanii po radiatsionnoy khimii, 1960 str. 65 (Theses of the Reports on the 2nd All-Union Conference of Radiation Chemistry, Moscow, 1960, p. 65) Ref. 1). The

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publications show (S. S. Medvedev, A. D. Abkin, P. M. Khomikovskiy, G. N. Gerasimov, V. F. Gromov et al., Vysokomolek. soyed. 2, 904, 1960, Ref. 2) that ethylene under similar conditions is polymerized more slowly. This difference in the polymerization rates of ethylene tetrafluoride and ethylene may be due to a slower rupture of chains by recombination in the polymerization of ethylene tetrafluoride due to repulsive forces. The latter occur in the approximation of perfluorinated radicals of polyethylene tetrafluoride. The slow rate of chain ruptures may also be due to topochemical peculiarities occurring in the polymerization of ethylene tetrafluoride. [Abstracter's note: this is a full translation from the original.] There are 2 Soviet-bloc references.

SUBMITTED: October 29, 1960

25263 S/190/61/003/007/007/021
B101/B208

15 8610

AUTHORS: Arest-Yakubovich, A. A., Gantmakher, A. R., Medvedev, S.S.

TITLE: Conditions of the formation of metalaromatic initiators of polymerization

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 7, 1961, 1003-1009

TEXT: The paper deals with the problem of catalytic polymerization, initiated by electron transfer from the atom of the alkali metal to the molecule of an aromatic compound which has a sufficiently high affinity to the electron: $Me + Ar \rightleftharpoons Me^+ + Ar^-$ (1). The general conditions were studied for the course of this reaction, in order to synthesize metal-aromatic complexes of different structure and to study the polymerization mechanism in the presence of such initiators. All operations were performed either in high-vacuum or anhydrous and oxygen-free nitrogen atmosphere. The following results are given: 1) Interaction between alkali metals and aromatic compounds in hydrocarbon medium. To prevent inactivation of the metal by a film from the reaction products with the

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aromatic compound, the experiments were carried out above the melting point of the metal. Sodium gave at 110-120°C in octane or toluene no reaction products with naphthalene or phenanthrene, even after 5-8 hr. With anthracene, Na gave at this temperature a red-violet, at 140-160°C a black powder. This product was completely soluble in tetrahydrofuran (THF) and triethylamine (TEA). These solutions had a characteristic color. The eutectic alloy of K with Na (85% K) quickly reacted with naphthalene and diphenyl at room temperature in hydrocarbon medium. Gray-black powders were formed. No reaction took place in the presence of benzene. In general, however, metalaromatic complexes will also be formed in non-electron-donor medium, if the metal has a low ionization potential and the hydrocarbon a high affinity to the electron. 2) Reactions in TEA medium. Lithium forms with naphthalene a cherry-red solution at room temperature. No reaction was observable with diphenyl even after 10 days. Na with phenanthrene gives only weakly colored solutions, but, with anthracene, quickly a solution which was green in the reflected light, and red in the transmitted light. A greenish-black film is formed on K under the action of naphthalene, which was insoluble in TEA. 3) The metalaromatic complexes were isolated after reaction in THF medium by filtering and subsequent

evaporation of the solvent in the high vacuum. Sodium-naphthalene decomposed after removing THF to give its initial components, sodium-anthracene was stable. In the complex of potassium-naphthalene, a black powder, the K/naphthalene ratio was 1.1. In the case of lithium-naphthalene, THF could not be completely removed. This is explained by the property of Li to form complexes with ethereal (oxygen-containing) solvents. 4) The initiating effect of metalaromatic compounds was studied on polystyrene. In the presence of Na-naphthalene, polymerization proceeded very quickly not only in pure THF, but also in toluene + 2-4 THF. In the presence of Na-anthracene (about 10^{-3} mole/l) polymerization in toluene - TEA = 1:1 proceeded slowly at 25°C, but was accelerated by a temperature rise. Na-anthracene initiates styrene polymerization also in inert medium (toluene). The solid sodium-aromatic complex dissolves, and the reaction rate increases more and more. 5) To estimate the probability of an interaction between alkali metal and aromatic compound forming soluble products, the following equation is discussed.
$\Delta E = - L - I + A + S_c + S_a + \ldots$ (4), where ΔE denotes the change in energy in the reaction, L the sublimation heat of the metal, I its ionization

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potential, A the affinity of the aromatic compound to the electron, S_-, S_a the solvation energy of the cation and anion, respectively, and , the energy of the coulomb interaction between the latter two. Basing on published data the following is written for the formation rate of metal-aromatic complexes. Li < Na < K; benzene < diphenyl < naphthalene < < phenanthrene < anthracene. But in some cases the cation of lithium reacts more intensely than K and Na, owing to solvation. A figure illustrates schematically the conditions for the formation of metalaromatic complexes. There are 1 figure, 2 tables, and 29 references 9 Soviet-bloc and 18 non-Soviet-bloc. The 4 most important references to English-language publications read as follows: M. Szwarc, M.Levy, R.Milkovich, J.Amer.Chem.Soc., 78, 2656, 1956; D.H. Richards, M.Szwarc, Trans. Faraday Soc., 55, 1644, 1959; J.P.V. Gracey, A.R. Ubbelohde, J.Chem.Soc., 1955, 4089; R.M. Hedges, F.A.Matsen, J.Chem.Phys., 28, 950, 1958.

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15.9201 1372, 1436, 1474

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S/190/61/003/011/015/016
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AUTHORS: Ushakov, V. D., Mezhirova, L. P., Galata, L. A., Kostyuk, A. G., Khusnutdinova, Z. S., Medvedev, S. S., Abkin, A. D., Khomikovskiy, P. M.

TITLE: Polymerization of styrene and butadiene with styrene in emulsions under the action of initiating redox systems. I. Effect of the nature of peroxide compounds on the rate of polymerization

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 11, 1961, 1716-1722

TEXT: Aim of the present work was the determination of the most active initiating redox systems for the polymerization of butadiene with styrene in emulsions, and especially of the effect of the nature of peroxides on the rate of polymerization. Nekal with 20 % of Na_2SO_4 and NaCl and mersolate (mixture of Na salts of sulfonic acids of the aliphatic series: $C_{15}H_{31}SO_3Na$) with $\leq$ 5 % of NaCl served as emulsifiers. Peroxides were used

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Polymerization of styrene and...

as oxidants (Table). Potassium ferrocyanide and ferrous pyrophosphate complex (IV) served as reducing agents. The rate of polymerization was determined either dilatometrically or from the yield of polymer (in ampules). Polymerization took place at 5°C with an excess of butadiene, styrene with peroxides dissolved in it (10 % solution), and the calculated amount of emulsifier solution. A suspension of the ferrous pyrophosphate complex was added at a certain temperature by means of medical syringes. Sub Va [illegible] used: (1) mercolate (5 % by weight added to water, ratio monomer : emulsifier 1 : 5); (2) potassium ferrocyanide. The temperature was varied between 0 and 40°C. Seven peroxides were investigated in amounts equivalent to 0.02 and 0.1 % by weight of isopropyl benzene hydroperoxide. $K_4Fe(CN)_6$ [illegible] in concentrations equimolecular to hydroperoxide. P-tert-butyl isopropyl benzene hydroperoxide (I) had the optimum rate of polymerization; that of diisopropyl benzene peroxide, isopropyl benzene- (II), and tert-butyl benzene hydroperoxide was lower, that of dibenzyl hydroperoxide still lower, and that of benzoyl peroxide the lowest. Polymerization with H_2O_2 proceeds fast at the beginning, then it decreases strongly, since H_2O_2 and the reducing agent are readily soluble in water. With 0.2-0.5 % by weight

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of II, only the initial rate increases. The total yield is lower than with 0.1 % by weight of II. Between 0.75 and 1 % by weight of II, initial rates and total yield are much lower. With 0.02-0.2 % by weight of I, initial rates increase. Since the total rate decreases at 0.2 % by weight, the dependence of the reaction rate on the hydroperoxide concentration is probably linked with the inhibiting effect of the decomposition products of hydroperoxide. With 0.1 % by weight of I and an equimolecular amount of $K_4Fe(CN)_6$, both total yield and initial rate increased with increasing temperature. The activation energies were determined according to the Arrhenius equation and found to be: E = 8.6 kcal/mole for II and E = 5.7 kcal/mole for I. Reduction of E by 3 kcal/mole at ~ 0°C corresponds to a 200-fold increase of the reaction rate. Since the rate is twice as high at 0°C, the pre-exponential factor in the Arrhenius equation increases by 10^2 times with decreasing activation energy of I. For the copolymerization of butadiene with styrene (ratio 70 : 30) at 5°C, the following was used: Nekal (2.8 and 1.4 % by weight added to water). 0.44 % by weight of ferropyrophosphate (related to iron sulfate) of the monomer. The ratio organic phase : aqueous phase was 1 : 4 (by weight). In the case of 0.34 %

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by weight of hydroperoxide of II (equimolar ratio to the monomer) optimum rate was achieved with IV. The highest yield was achieved with aryl-alkyl hydroperoxides (I and 1,1-diphenyl ethane hydroperoxide (III)) (Table). With an emulsifier concentration of 2.8 %, maximum conversion (70-75 %) was achieved after 7 hr with 0.2 % by weight of I and with 0.3 % by weight of III. With 0.54 % by weight of II, optimum conversion (~50 %) was achieved after 2 hr. Polymerization of I and IV with 1.4 or 2.8 % by weight of emulsifier was constant up to 30 % conversion, then the rate dropped. With 1.4 % by weight, the initial rate was lower and the decrease more distinct. With an addition of 0.1 % by weight of hydroperoxide + 0.26 % by weight of IV (after 1 hr new addition of 0.1 % by weight of hydroperoxide and 0.18 % by weight of IV), constant polymerization took place up to 60 % conversion. Thus, the consumption of the initiating system causes a decrease in rate. The efficiency of redox systems and initiators depends on the reactivity of the radical as well as on the solubility of the peroxide compounds in the aqueous phase and in the monomers. The lower the solubility in water, the lower the loss and the stronger the initiating action. I + IV cause a higher rate of reaction than II + IV due to lower activation energy and lower solubility in water. For II + IV, the redox reaction occurs at the

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pnase boundary, for I + IV also in the aqueous phase. The existence of a maximum of the rate of polymerization for I and butyl isopropyl hydroperoxide is caused by polymerization inhibition due to the decomposition products of the hydroperoxides. The authors thank A. G. Pod"yapol'ska for help with experiments and T. I. Yurzhenko (L'vovskiy industrial'nyy institut (L'vov Industrial Institute)) for supplying some hydroperoxides. There are 5 figures, 1 table, and 7 references: 4 Soviet and 3 non-Soviet. The two references to English-language publications read as follows: F. A. Bovey, I. M. Kolthoff, Emulsion Polymerization, New York, 1955; C. P. Fryling, Industr. and Engng. Chem., 41, 986, 1949.

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11,2211

AUTHORS: Ushakov, V. D., Mezhirova, L. P., Galata, L. A., Kamalutdinova, Z. S., Sheynker, A. P., Medvedev, S. S., Abkin, A. D., Khomikovskiy, P. M.

TITLE: Polymerization of styrene and butadiene with styrene in emulsions under the action of initiating redox systems. IL Effect of the nature of the reducing agent on the rate of polymerization

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 11, 1961, 1725-1729

TEXT: The effect of the reducing component of initiating systems and of the addition of a second reducing agent on the rate of polymerization is studied. Used were systems of hydroperoxides (HP) of isopropyl benzene (I) or p-tert-butyl isopropyl benzene (II) with ferropyrophosphate complex (III), potassium ferrocyanide (IV), ferrous sulfate with o-phenantnroline, or of complexes of α,α-dipyridyl with ferrous oxalate. Sodium bisulfite and the bisulfite compound of acetone served as reducing

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